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HIGH TEMPERATURE THERMOELECTRIC PERFORMANCE OF NANO-SCALE MISFIT-LAYERED $Ca_3Co_4O_9$ WITH Ga SUBSTITUTION

N. V. Nong[1], J. Xu[1], S. Yanagiya[1], N. Pryds[1] and M. Ohtaki[2]

[1]*Fuel Cells and Solid State Chemistry Division, Risø DTU, 4000 Roskilde, Denmark*

[2]*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Fukuoka, 816-8580, Japan*

Email: ngno@risoe.dtu.dk

In recent years, nano-scale misfit-layered $Ca_3Co_4O_9$ oxide has been attracting a considerable attention since single crystal of $Ca_3Co_4O_9$ was found to exhibit a large thermoelectric (TE) performance (*ZT* reaches ~0.87 at 973 K). This compound is high thermal stability and lack of toxicity, considering as a good material for thermoelectric power generation at high temperatures. However, single crystal samples are too small to be used in the fabrication of the TE devices. More feasible method is to use polycrystalline materials and enhance their TE properties. Besides the improvement on the nanostructure and preparation techniques, chemical substitution is also an effective method to enhance the *ZT* value. In this study, a series of nano-scale misfit-layered Ga-substituted osxides $Ca_3Co_{4-x}Ga_xO_{9+\delta}$ (x = 0, 0.05, 0.1, and 0.2) were prepared by solid-state reaction, followed by hot-pressing and their thermoelectric properties were investigated from 300 to 1200 K. Partial Ga substitution leads to simultaneous increase of the electrical conductivity and thermopower of $Ca_3Co_{4-x}Ga_xO_{9+\delta}$ (see Fig. 1). The ZT value for the x = 0.05 sample is 71.4% higher than the undoped one at 1073 K (see Fig. 2). Along with the unique feature that $Ca_3Co_4O_{9+\delta}$ consists of the two sublattices of Ca_2CoO_3 and CoO_2 with one metallic and the other activated conduction, these results seem to suggest that this feature provides an avenue to improve the thermoelectric performance by partial substitution in the Co site within the sublattice having activated conduction.

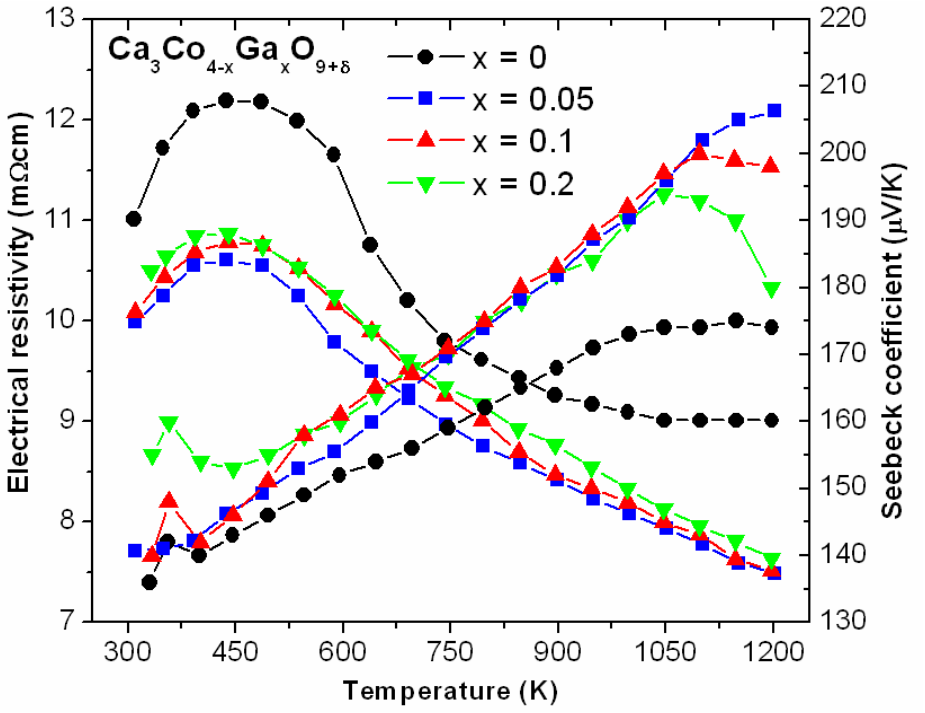

Fig. 1. The electrical resistivity and Seebeck coefficient as a function of temperature for $Ca_3Co_{4-x}Ga_xO_{9+\delta}$(x = 0, 0.05, 0.1, and 0.2) samples.

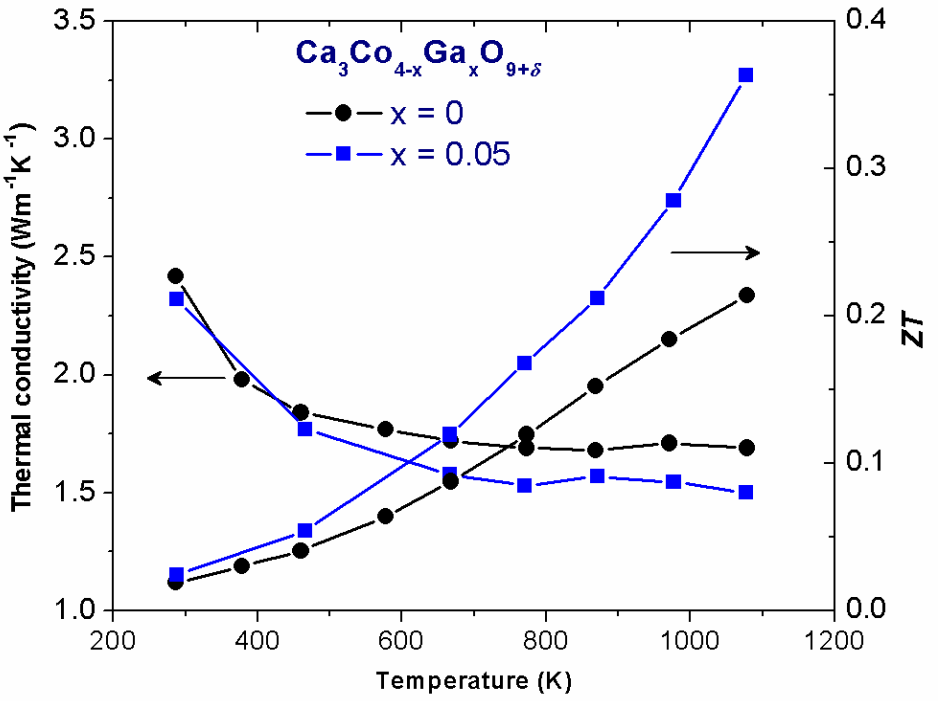

Fig. 2. Temperature dependences of the thermal conductivity and the dimensionless figure of merit ZT for $Ca_3Co_{4-x}Ga_xO_{9+\delta}$ samples with x = 0 and 0.05.